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Observations on the Rare Earths

Chemistry

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OBSERVATIONS ON THE RARE EARTHS

BY

EDWARD WICHERS

A. B. Hope College, 1913

THESIS

Submitted in Partial Fulfillment of the Requirements for the

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June 1915.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY Edward Wichers,

ENTITLED Observations on the Rare Earths

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF Master of Science in Chemistry

Clarence W. Backe
In Charge of Thesis

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Head of Department

Recommendation concurred in:*

_____ } Committee
on
Final Examination*

*Required for doctor's degree but not for master's.

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OBSERVATIONS ON THE RARE EARTHS.

INTRODUCTION.

The chief problem which has stood in the way of the development of the chemistry of the rare earth metals has been that of finding adequate methods for the separation of the elements comprising the group. For this reason, these elements have been, up to the present time, of little other than purely scientific interest. However, the comparatively recent discovery of many important industrial uses for other of the rarer elements, hitherto also considered of interest only in the laboratory, indicates the probability of finding for the rare earth metals uses which will be no less important. They occur in greater abundance in nature than do many of the other rare elements which have already attained commercial importance, but the supply cannot be used until a better understanding of the properties of the elements and their compounds leads to their demand in the arts and industries.

In order that a study of the properties of the rare earth elements may be properly made, methods for the isolation of the individual members of the group must first be developed. Thus far, fractional crystallization and fractional precipitation have been the methods principally employed. More recently some work has been done on the fractional electrolysis of the salts. Of the

L. M. Dennis and B. J. Lemon. - J. Am. Chem. Soc., 37, 131, (1915)

the two first named methods of separation, that of fractional crystallization has proven in general the more satisfactory because it permits of handling larger quantities with more rapidity, and less loss of material, than does the other. In certain cases, however, fractional precipitation gives a more rapid separation. One of the great difficulties with the methods of fractional crystallization now in use is that the rate of separation is not uniform. In the case of the Yttrium group bromates, for example, the first crystallizations give a relatively rapid separation for certain elements in the group, but a very long-continued fractionation is necessary to raise the degree of purity from this point. It is with this in mind that new compounds, with the widest possible range of solubility between the several elements of the group, must be sought for.

The work described in the following paragraphs is a part of that being done in this department under the general plan of preparing a complete series of double sulphates, selenates, and tellurates of the rare earths with the alkali metals and with certain stable organic bases, with a subsequent study of their solubility and other properties. The double sulphates with potassium and sodium have already been used with some success in the separation of the elements, especially in the separation on a large scale of the Cerium and Yttrium groups. The idea suggests itself that among the double selenates and tellurates, certain salts may be found with marked difference in solubility. This paper describes work done in general on the separation and purification of the elements of the Cerium group, and in particular the work done toward the preparation of the double selenates of lanthanum and neodymium with benzylamine, lithium, and caesium.

SEPARATION AND PURIFICATION OF CERIUM GROUP ELEMENTS.

Lanthanum and Neodymium - The elements of the Cerium group were obtained chiefly from material supplied by the Welsbach Company in the form of double sulphates of sodium with (principally) the Cerium group metals. This material was decomposed by boiling with strong sodium hydroxide solution. The resulting hydroxides were washed comparatively free from sodium. The cerium was removed by oxidation with potassium bromate. The cerium free material was again precipitated as hydroxides, washed, and dissolved in nitric acid. The proper amounts of magnesium oxide and nitric acid to form the magnesium double nitrates were then added to the solution. This solution was subjected to a series of fractional crystallizations until the best practicable separation between lanthanum and neodymium was obtained. The lanthanum magnesium nitrate, free from all but very slight traces of neodymium was set out to be converted later to the ammonium double nitrates to complete the separation between the lanthanum and praseodymium. The fractionation of the remainder of the series was continued to obtain neodymium free from praseodymium and the elements of the more soluble end (samarium, etc.). The neodymium material ultimately used was taken out after no change of color could be detected in several fractions in the middle part of the series.

Cerium - Cerium was obtained from a large quantity of mixed ceric and manganic oxides together with hydroxides of lanthanum, neodymium, etc., resulting from the separation of cerium from the

other metals of the cerium group by oxidation with potassium permanganate, a method which has since been discarded in favor of the potassium bromate oxidation. These oxides and hydroxides were dissolved in concentrated hydrochloric acid, with copious evolution of chlorine, and the rare earths precipitated from the acid solution with oxalic acid. One precipitation gave oxalates very nearly free from manganese. These oxalates were washed, dried, and dissolved in concentrated nitric acid with complete oxidation of the oxalic acid.

With regard to the decomposition of rare earth oxalates with nitric acid it was observed that material with a high cerium content passed into solution very readily, so that the method was a convenient one for converting the oxalates to the nitrates. Pure lanthanum oxalate, however, as well as the oxalates of the material rich in gadolinium, and again in the case of the praseodymium, was found to dissolve with extreme difficulty, so that these oxalates could not be converted to nitrates by this means. The conditions determining the solubility of oxalates in nitric acid were not investigated further.

The solution of the nitrates was nearly neutralized with ammonium hydroxide and the cerium removed by the potassium bromate oxidation method described by James and Pratt.* The method consists of boiling the nitrate solution with potassium bromate in the presence of lumps of marble. In removing cerium from other material in which it was present only in small quantity, no difficulty was experienced, all of the cerium being precipitated as ceric basic nitrate or bromate in a short time. With this material,

*James and Pratt. - J. Am. Chem. Soc., 33, 1326, (1911).

containing a high percentage of cerium, it was found necessary to boil the very concentrated solution vigorously for many hours, care being taken to replenish the lumps of marble as they dissolved, in order to prevent the solution from turning acid, with the subsequent reaction between the hydrobromic and bromic acids present. A Fletcher burner supporting a granite enamelled iron pail, over which was placed a five litre constant-level flask, was found to be the most suitable apparatus. To obtain cerium as nearly as possible free from the other earths, the precipitate of basic ceric nitrates and bromates was removed before the separation was complete. The basic ceric compounds were washed with hot water containing three percent ammonium nitrate, to prevent the precipitate from becoming colloidal. The wash solution continually showed a slight precipitate with ammonia, showing the basic compounds to be slightly soluble, but the amount dissolved was negligible. This cerium material still showed traces of neodymium lines in the absorption spectrum of a concentrated solution. To finally purify the cerium, the basic nitrate and bromate were dissolved in concentrated nitric acid with a small amount of alcohol, as directed by James, and reprecipitated by diluting the solution and boiling with marble.

Praseodymium - The praseodymium was obtained from the incomplete series of fractional crystallizations: a bromate series, a manganese double nitrate series, and an ammonium double nitrate series, the last two of which showed some cerium, besides containing lanthanum and neodymium. The earth from the bromate series was precipitated as hydroxide with potassium hydroxide and later as

oxalate with oxalic acid, and finally ignited to the oxide. The manganese series was precipitated with oxalic acid in acid solution, to remove the manganese, and the oxalates dissolved in concentrated nitric acid, after which the cerium was removed by the method already described, and the earths precipitated as oxalates, followed by ignition to the oxides. All the oxides were united, dissolved in nitric acid and ammonium nitrate added in the proportion to form the ammonium double nitrates. The solution was subjected to fractional crystallization to separate the praseodymium from the lanthanum and neodymium.

Gadolinium - Gadolinium was obtained from two incomplete series: one of the nickel double nitrates, and the other of the magnesium double nitrates containing bismuth nitrate. From the first the earths were precipitated by ammonium hydroxide in excess, and later as oxalates, the oxalates finally being ignited to oxides. From the other the bismuth was precipitated by hydrogen sulphide and the earth was then precipitated from a decidedly acid solution by means of oxalic acid. This precipitation did not remove all traces of magnesium but gave a product sufficiently pure for fractional crystallization. The oxalates were ignited to oxides and the combined oxides then dissolved in bromic acid (obtained from barium bromate and sulphuric acid), and prepared for fractionation.

PREPARATION OF MATERIALS.

Selenic Acid - The selenic acid used was prepared as follows: The best selenium available was dissolved in nitric acid, the solution evaporated, the residue taken up in water and the selen-

ium reprecipitated by means of sulphur dioxide. This selenium was washed, again dissolved in nitric acid and the residue which was left after evaporation sublimed at a moderate temperature. The sublimed selenium dioxide showed a pure white color except for a tinge of pink in some portions, probably due to a slight dissociation to selenium. The dioxide was dissolved in water, the solution filtered from any selenium and neutralized with ammonium hydroxide. To this solution silver nitrate solution was added, precipitating silver selenite. The precipitate was washed and the suspension in water treated with bromine until the solution acquired a permanent yellow color. This reaction yielded silver bromide and selenic acid. The acid was filtered off, concentrated by evaporation, and used in the subsequent preparation of the selenates of lanthanum, neodymium, benzylamine, lithium and caesium.

Lanthanum selenate - The lanthanum oxide used was taken from material still containing cerium, owing to an incomplete cerium separation by the potassium permanganate method. The ammonium double nitrates were fractionated until crystals were obtained, the mother liquor from which showed no trace of absorption bands in the spectrum through a seven centimeter layer. The solution still contained a small amount of cerium which was removed by the potassium bromate oxidation method previously described. The solution was boiled with potassium bromate in the presence of marble until the addition of hydrogen peroxide to the faintly ammoniacal solution showed no yellow coloration in the precipitate, even upon standing for an hour or longer. The lan-

thanum was precipitated from this solution with ammonium hydroxide in the presence of ammonium chloride. The hydroxides were repeatedly precipitated and washed until only very slight traces of magnesium could be detected. With this material as well as with the neodymium material it was found very difficult to remove all of the magnesium. After many precipitations, slight traces of magnesium were still present, probably owing to absorption phenomena. After the final precipitation with ammonium hydroxide, the lanthanum was precipitated as oxalate, with oxalic acid, and the oxalate was then ignited to the oxide. The selenate was prepared by dissolving the oxide in selenic acid.

Neodymium selenate - The neodymium oxide was purified from the common elements in the way already described for lanthanum. In the washing of the hydroxides of neodymium, and lanthanum as well, it was observed that the addition of ammonia to the wash water was effective in restraining the marked tendency of the hydroxides to become colloidal. The selenate was prepared by the solution of the oxide in selenic acid.

Lithium selenate - Lithium selenate was prepared by dissolving the best lithium carbonate available, in selenic acid.

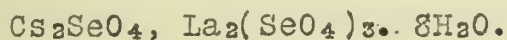
Benzylamine selenate - Benzylamine selenate was prepared by the neutralization of the amine with selenic acid.

Caesium selenate - The caesium was obtained from pollucite, from Maine. Ten pounds of the mineral was ground to pass a hundred mesh sieve and decomposed with strong hydrochloric acid. Antimony trichloride was added to the acid solution, precipitating the double chloride of caesium with antimony. This compound was

decomposed with ammonium hydroxide and the hot solution of caesium chloride in hydrochloric acid treated with iodine until no more iodine dissolved. On cooling this solution, yellow caesium di-chloriodide crystallized out. This salt was twice recrystallized, with centrifugal drainage. The dichloriodide was decomposed to the chloride by heat, and the chloride heated with sulphuric acid until only a very slight trace of hydrochloric acid remained. The solution of the acid sulphate and the excess sulphuric acid was treated with barium hydroxide solution in slight excess and then with carbon dioxide to remove the excess barium. The resulting caesium carbonate solution was neutralized with selenic acid, giving caesium selenate.

PREPARATION OF SALTS.

Caesium, Lanthanum Double Selenate.



Caesium selenate and lanthanum selenate were added together in solution in approximately equi-molecular proportions. The solution was first concentrated on the steam bath to a point where the lanthanum selenate which crystallized out of the warm solution would just redissolve at room temperature. The solution was further evaporated by blowing dry filtered air thru it at room temperature until crystals commenced to form, at which point the solution with the few crystals was placed in a vacuum desiccator over sulphuric acid. After a few days a considerable mass of well-defined crystals had separated from the concentrated solution. These were removed from the solution and thoroughly centrifuged,

washed with a few drops of water, and again centrifuged. Examination showed the crystals to be monoclinic prisms.

In the analysis of this compound the selenium was first determined by boiling a weighed portion of the salt with concentrated hydrochloric acid, thereby reducing the selenic acid to selenious acid. The selenium was precipitated from the strongly acid solution with sulphur dioxide, filtered on a Gooch crucible, washed with water, dried at 150° and weighed. The lanthanum was determined by precipitating the hydroxide from the filtrate from the selenium, after evaporating off the excess of hydrochloric acid. The hydroxide was filtered upon paper, washed, dried and ignited with the paper in platinum crucibles, in the blast lamp. The lanthanum was also determined in a new sample of the salt by precipitating the hydroxide from the solution without previously precipitating the selenium, and igniting with the filter paper, in platinum crucibles, in an electric muffle furnace. Constant results could not be obtained either with lanthanum or later with neodymium, and in all cases the percentage of oxide ran much higher than that calculated from the formula which accorded to the analytical results obtained in the determination of selenium, caesium, and water of hydration. The oxide ignited in the blast lamp yielded a considerable precipitate with barium chloride in acid solution, having evidently absorbed oxides of sulphur from the gas flame. It was intended to attempt the determination of the earth by precipitating the oxalate, dissolving the precipitate in sulphuric acid and titrating the oxalic acid with potassium permanganate, but it was impossible to make the determination at that time.

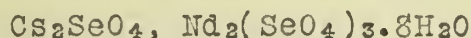
The cause of the error in the determination as oxide from the hydroxide is also to be studied further.

Caesium was determined in the filtrate from the precipitation of the lanthanum by evaporating to dryness, addition of sulphuric acid, and ignition to sulphate in a gas muffle at a bright red heat. Water of hydration was determined by heating a sample of the salt in an electric oven. At 150° about ninety percent of the water was lost and the dehydration was apparently completed at 250°. The anhydrous salt showed no decomposition at this temperature, nor on heating to dull redness for a short time.

ANALYSIS.

Theory		Found
25.86	La_2O_3	31.98
22.34	Cs_2O	22.01
40.37	SeO_3	39.77
11.43	H_2O	11.31

Caesium, Neodymium Double Selenate.



The caesium neodymium double selenate was prepared in the same way as that described for the lanthanum salt. The two salts were apparently isomorphous. The same analytical methods were employed and the following results were obtained:

Theory		Found
26.48	Nd_2O_3	32.74
22.16	Cs_2O	21.36
40.03	SeO_3	39.47
11.33	H_2O	11.19

The conformity of the analytical with the calculated results for the caesium, selenium, and water of hydration warrants the assumption that the high result for the rare earth oxide is due to an error in the analytical method, and that the formulas assigned represent the composition of the salts.

Lanthanum and Neodymium Selenates.

In an attempt to prepare the double lithium selenate with lanthanum and neodymium masses of minute, silky, needle-shaped crystals separated from the concentrated solution. Upon qualitative analysis it was found that these contained no lithium. The crystals, however, did not correspond in appearance to the selenate of lanthanum reported in the literature (no selenate of neodymium has yet been reported), and were apparently crystals of hydrated selenates with a different amount of water from the selenate of lanthanum already known. Attempts at this time to determine accurately the water of hydration were not successful.

Crystals apparently identical with those just described separated from concentrated solutions containing approximately equimolecular proportions of benzylamine selenate and lanthanum and neodymium selenates.

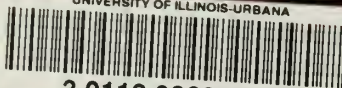
It is probable that the double selenates of lithium and of benzylamine with the rare earths can be prepared by using a solution containing an excess of lithium and benzylamine selenates.

The writer wishes to express his indebtedness to Professor C. W. Balke, under whose careful assistance and direction this work was carried out.





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